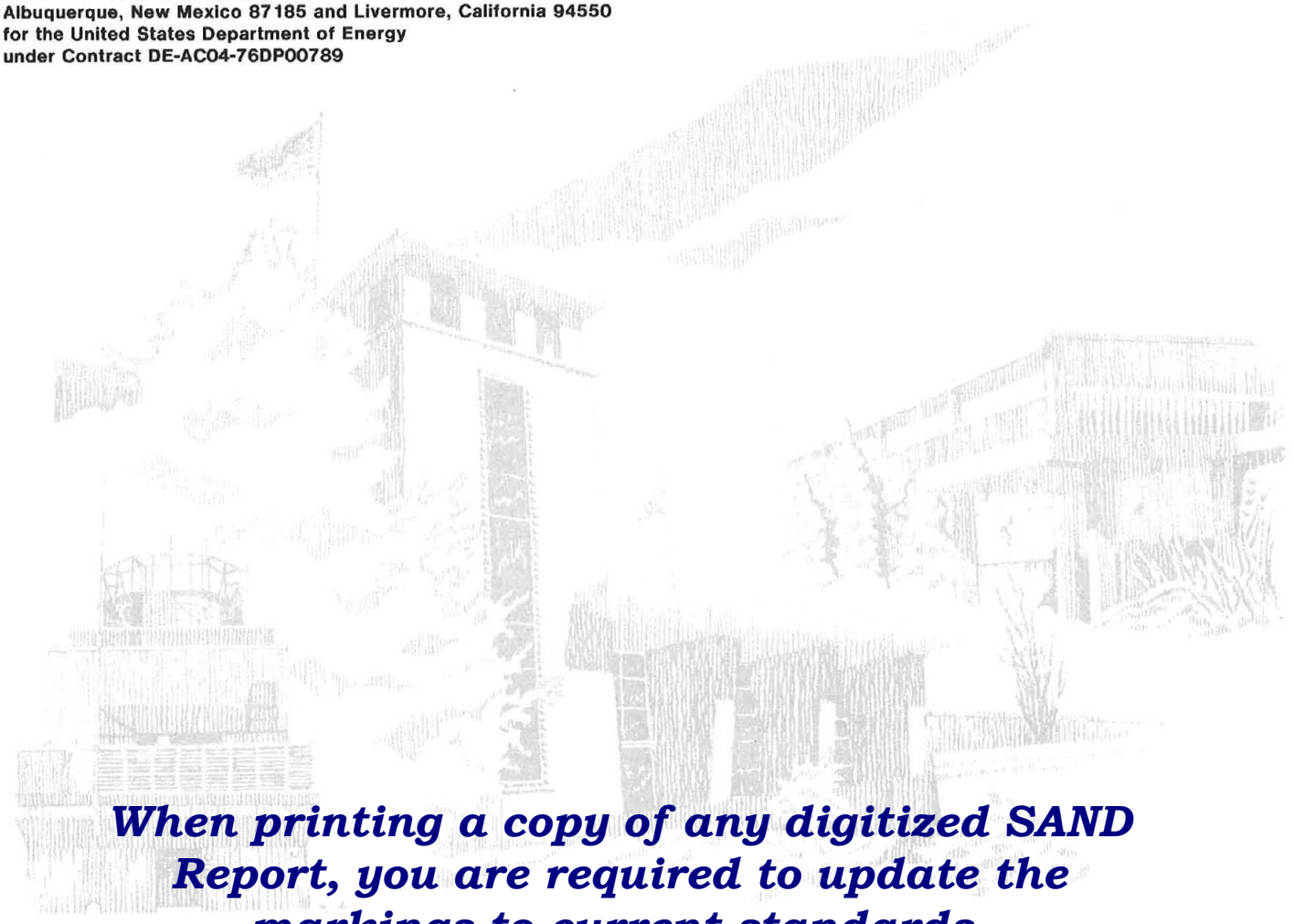
SANDIA REPORT

SAND86—2822 • UC—25
Unlimited Release
Printed December 1988

Barrier Anodic Coatings Formed on 6061-T6 Aluminum Alloy in Electrolytes Containing Different Ethanol to Water Ratios

Janda K. G. Panitz, Donald J. Sharp, F. Edward Martinez,
Raymond M. Merrill, Kenneth J. Ward

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789



Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A07
Microfiche copy: A01

SAND86-2822
Unlimited Distribution - UC-25
Printed December 1988

BARRIER ANODIC COATINGS FORMED ON 6061-T6 ALUMINUM ALLOY IN ELECTROLYTES CONTAINING DIFFERENT ETHANOL TO WATER RATIOS

Janda K. G. Panitz
Surface & Interface Technology

Donald J. Sharp
Interfacial Chemistry & Coating Research

F. Edward Martinez
Metallurgical Process Division
(Plating and Coating Section)

Raymond M. Merrill
Analytical Chemistry Division

Kenneth J. Ward
Surface Chemistry & Analyses Division

Sandia National Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

We have studied barrier anodic film formation on 6061-T6 aluminum alloy substrates as a function of electrolyte composition for five mixtures of ammonium tartrate dissolved in water and diluted with different amounts of ethanol. The ethanol: water ratios that were used included

1. 98% ethanol, 2% water;
2. 80% ethanol, 20% water;
3. 40% ethanol, 60% water;
4. 10% ethanol, 90% water;

and 5. 100% water.

High resistivity (60-120 kΩ cm) mixtures were studied. The effects of electrolyte temperatures within the range of 18°C to 38°C were explored. During processing, we typically maintained a constant current density of 1 mA/cm^2 until a cell voltage of 950 V had been achieved; we then held the cell voltage fixed while the current diminished to 0.05 or to 0.10 mA/cm^2.

The results of this study indicate that the best dielectric coatings and the shortest processing times occur for the 100% water-ammonium tartrate electrolyte. The second best coatings and processing times occur in conjunction with the use of 98% ethanol, 2% water plus ammonium tartrate electrolyte. In general, visibly flawed coatings, scintillation events at cell voltages in excess of approximately 750-800 volts and/or abnormally long processing times occur in conjunction with the use of electrolyte mixtures containing 20%, 60%, and 90% water.

We analysed samples of electrolyte as a function of usage, and evaluated the composition of the coatings using Fourier Transform Infrared Analysis to better understand the mechanisms which contribute to anodic coating growth that result in the observed variations in the dielectric properties. All of the coatings exhibited similar compositions except with regard to the amount of CO_2 that was physisorbed in the coatings. The dielectrically inferior coatings that were typically produced by the electrolytes containing ethanol contain substantially more CO_2 than the coatings grown in the 100% water-based electrolyte. These results strongly suggest that the ethanol in the electrolyte oxidizes and forms CO_2 which is incorporated in the coatings and results in inferior dielectric properties.

TABLE OF CONTENTS

FIGURES

Figure 1. Large flaws in a coating grown in an electrolyte mixture comprising 60% water, 40% ethanol. Continual and dense scintillation events were observed over the surface of this coupon during anodization.

Figure 2. FTIR spectra displayed by the anodic coatings. a. Coating formed in a 90% water 10% ethanol mixture. b. Coating formed in a 100% water mixture. c. Coating formed in a 98% ethanol mixture. Here the 2343 cm^{-1} band is assigned to physisorbed CO_2; the 1570 cm^{-1} and 1470 cm^{-1} doublet to a carboxylate group; the 950-980 cm^{-1} band to $A\ell_2O_3$; and the broad band at 680-750 cm^{-1} is assigned to a carboxylate bending vibration superimposed with $A\ell$-O transverse optical lattice vibration.

Figure 3. SEM micrographs showing profiles which were used to determine the thicknesses of the coatings that were formed at 950 V and aged-in to 10% of the maximum current density. 98% ethanol at 18 ± 2°C produces coatings that are 1.2 μm thick. b. 98% ethanol at 21°C increasing to 35°C during the voltage rise, and 35°C decreasing to 21°C during age-in produces 1.4 μm thick coatings. c. 98% ethanol 21°C increasing to 35°C during the voltage rise and 35 ± 2°C during the age-in-1.3 μm thick coatings. d. 98% ethanol, 35 ± 2°C - 1.2 μm thick coatings. e. 100% water at 16 ± 2°C produces coatings that are 1.4 μm thick. f. 100% water at 25 ± 4°C - 1.4 μm thick coatings. 100% water at 33 ± 4°C - 1.2 μm thick coatings. The mottled, dark and light grey region representing areas characterized by low electron emissivity is interpreted as being the barrier anodic layer. The brighter region of higher electron emissivity which appears to cover the anodic coatings in views 1-3 is aluminum rather than gold according to energy dispersive analysis. It may be an artifact of the sample preparation techniques that were used.

Figure 4. Surface morphologies of coatings imaged using transmission electron microscopy. a. Artifact of an alloying precipitate etch pit-100% water coating. b. Crystallite with 6-fold rotational symmetry - 100% water coating. c. Micrograph taken at a lower magnification showing the relative abundance of these features for a 100% water coating. d. Similar magnification as shown in e, showing the relative abundance of etch pits artifacts and other flaws and the absence of crystallites for a 98% ethanol coating.

Figure 5. Processing time for different electrolyte temperatures.
a. 98% ethanol mixture. b. 100% water mixture.

Figure 6. Breakdown voltages exhibited by coatings formed at different temperatures. a. 98% ethanol coatings. b. 100% water coatings.

Figure 7. Increase in the resistivity of the 100% water mixture as a function of repeated use. The coatings were grown on 10 x 10 cm^2 coupons at 950 V and aged-in to 0.05 mA/cm^2. Each coupon represents approximately 7.4 x 10^5 mA-sec. passed through the 6ℓ bath with parallel plate counterelectrodes.

BARRIER ANODIC COATINGS FORMED ON 6061-T6 ALUMINUM ALLOY IN ELECTROLYTES CONTAINING DIFFERENT ETHANOL TO WATER RATIOS

I. INTRODUCTION

Barrier anodic processes are now extensively used by capacitor manufacturers to form cost-effective dielectric coatings on aluminum substrates. A list of the desirable characteristics of a process that is used in a barrier anodization facility might include the following attributes:

1. Produces good quality, stable dielectric coatings.
2. Short processing times.
3. Involves the use of (a) inexpensive, (b) readily available, noncontrolled, and (c) nonhazardous chemicals.
4. Reusable, yielding (a) reproducible consistent results with (b) little or no adjustment in chemistry, i.e., "doctoring."
5. Forgiving of instrument and geometry dependent fluctuations in agitation, bath temperature, current density and cell voltage.
6. Operates optimally at moderate temperatures.
7. Does not require extensive or complicated auxillary treatments, e.g. rinsing in nonaqueous solvents, annealing, cleaning, burning-in, sealing, etc.

In practice, it is difficult to understand and predict what combination of ingredients will result in an electrolyte with desirable processing characteristics.[1,2] Many reactions occur during anodization. It is difficult to monitor the most important mechanisms directly because they mainly occur in the double layer, a 20-30 Å thick region at the anode-electrolyte interface. During anodization, it is feasible to measure only macroscopic reactions which incorporate the more extensive diffusion zone, which, in turn, reflects only a simplistic model of the reactions that are occurring. Additional information can be inferred, in retrospect, by analysing samples drawn from the electrolyte and

coating properties after processing. Some fundamental properties of the double layer which probably are important with regards to anodic film formation include:

1. The concentration, mass transport, and identity of the chemical species present,
2. Polarization and capacitance
3. Electrical conductivity,
4. Thermal conductivity,

and 5. Thermal capacitance.

In the present study, we have taken an empirical approach and investigated the processing variations and coating properties associated with different mixtures of ethanol, water, and ammonium tartrate. Mixtures with higher concentrations of ethanol can be expected to have a more complex spectrum of organic species present in the double layer, less polarization, higher vapor pressures, lower thermal conductivity, and lower thermal capacitance when compared to mixtures containing more water. From the results of this study, we can qualitatively infer the effects that some of the intrinsic properties of an electrolyte have on anodic film formation.

II. EXPERIMENTAL

A. Substrate Preparation

We anodized 5 x 10 cm (0.050 cm thick) or 10 x 10 cm (0.150 cm thick) 6061-T6 aluminum alloy coupons which were scrubbed with a detergent and deionized water solution until all of the metal supplier markings and grease and oil blemishes were gone. The coupons were then treated with a sequence of standard etches:[3] a. 5% NaOH at 70-75°C for 5 min., b. 50% concentration HNO_3 at 20-22°C for 10 min. and finally, c. concentrated HNO_3 with 64 gm/ℓ NH_4HF_2 at 20-22°C for ten minutes. After being etched, the coupons were thoroughly rinsed in deionized water, then air dried. The final etchant was used immediately before (e.g. less than 30 min.) commencing electrolysis.

B. Anodization

1. Electrolyte Preparation.

We prepared our electrolyte mixtures from deionized water, absolute ethanol, and a solution of 2.5 gm reagent grade ammonium tartrate that was dissolved in 470 mℓ deionized (18 MΩ-cm) water. The desired volumes of water to ethanol were mixed to yield five to six liters of solution. Then some small volume of the ammonium tartrate and water solution was added so that a mixture with a resistivity of approximately 70 kΩ-cm at 21°C was obtained. The volume of ammonium tartrate solution that results in this desired resistivity varies from approximately 1:40 parts pure ethanol for the "98% ethanol" electrolyte, to 1:100 parts water for the "100% water" electrolyte.

Chloride ions at concentrations of the order of 500 ppb are known to interfere with anodic $A\ell_2O_3$ formation.[4] For this reason, we used ion chromatography to analyze the purity of our as-mixed electrolyte.[5] We subjected fresh mixtures of electrolyte to a number of preliminary anodization runs so that consistent, reproducible processing times were observed. This preliminary break-in of an electrolyte is commonly found to be necessary and is sometimes called "dummying the bath." The chloride ion contamination has been observed to decrease during these break-in runs. After a sufficient number of break-in runs had been performed, the processing behavior became more nearly reproducible and self-consistent. We then began to routinely record the processing characteristics, evaluate coating properties, and periodically draw samples of electrolyte for chemical analysis.

2. Apparatus.

We used three different anodization facilities for these experiments. We did most of our anodization runs in a large glass dessicator bowl which was equipped with a tightly fitting ground glass lid which was propped open with two, 2 cm thick teflon blocks during use. (This was done so that air could circulate freely through the cell during anodizaton. Otherwise, vapors from the electrolyte tended

to condense on parts of the anode above the level of the electrolyte, and resulted in extremely long processing times.) This cell typically contained 5-6 ℓ of electrolyte and two flat, parallel 10 cm x 10 cm platinized titanium mesh cathodes spaced 3.12 cm apart. During anodization, an aluminum alloy coupon was placed midway between these cathodes. The bowl contained a magnetic stirrer and a thermometer. It was placed in a large basin which was filled with warm water, or ice water so that the electrolyte temperature could be controlled during use. This apparatus was placed on a clean bench in a laboratory to reduce the chance of accidental chloride ion contamination.

A small number of anodization experiments were performed in another facility in a similar anodization cell of approximately the same geometry and dimensions. Repeated events resulting in inadvertant chloride ion contamination brought a premature end to barrier anodization experiments at this second facility.

A third anodization cell utilizing a 15 cm diameter, stainless steel beaker was also occasionally used for these experiments. This cell contained 2 ℓ of electrolyte; the walls of the beaker were biased negative and formed the cathode. Coupons, typically 10 cm x 10 cm in size, were suspended from a corner in a plane subtending the center of this cell. Copper tubing brazed to the outside of this cell provided cooling. The electrolyte was completely open and agitated during electrolysis. The cell was tightly covered when not in use.

Three types of power supplies were used in these experiments:

a. Two Sorenson DCR600-3B^{+} connected in series, or

b. A Kepco BHK 1000-02M, or

c. A Fluke 3330 B "Calibrator."

Two external Fluke 8000A multimeters measured current and voltage during anodization.

3. Electrolysis.

Before beginning a typical anodization run, we would turn on the magnetic stirrer and wait at least 3 min. before measuring the resistivity of the bath at

21-22°C. Then, depending on the temperature schedule that we chose to follow, we filled the basin surrounding the anodization cell with hot water or ice water and waited until the thermometer mounted in the electrolyte indicated that we had reached the desired temperature. We then immersed a fixed area of an aluminum alloy coupon in the electrolyte, attached the positive electrode from the power supply and commenced electrolysis at a fixed current density averaging 1 mA/cm^2. During this time we observed the increase in the cell voltage that was necessary to maintain this current density as the anodic coating grew and cell resistance increased. When the cell voltage reached 950 V, we crossed over from constant current to constant voltage operation. We maintained a cell voltage of 950 V and observed the rate of decrease in current density as the barrier coating continued to grow and the cell resistance continued to increase.

When the current had decreased to 10% of the maximum value (for the different electrolyte evaluation studies) or to 5% (for preliminary tests evaluating the effects of repeated usage on the 100% water electrolyte), we turned off the power supply, removed the coupon from the electrolyte, rinsed the coupon in 2 ℓ of deionized water at 21-22°C for 5-8 sec. and air dried the coupon.

C. Electrolyte Analysis and Coating Characterization.

At periodic intervals we collected 25 cc samples of electrolyte for chemical analysis to determine the changes that were occurring in conjunction with repeated usage. Ion chromatography was used to quantitatively analyze the anion species present.

Arrays of 1 mm diameter, 5000 Å thick gold dots were thermally evaporated over the surface of the barrier anodic coatings. The dielectric properties: breakdown voltage and capacitance were measured for these metal-anodic coating-metal capacitors at 21-22°C at the ambient relative humidity, 20-30%. The dielectric properties were observed by gently contacting a gold dot with a spring loaded platinum probe while a bare metal area on the coupon was connected to the opposite electrical lead. Breakdown voltage was observed for forward bias condi-

tions (aluminum positive) for a voltage ramp averaging 10 V/sec supplied by an RC circuit. Breakdown voltage was taken to be the maximum voltage that was recorded by a Fluke digital voltmeter model 77* before the coatings failed and the voltage went to 0. Capacitance was measured at 60 Hz with an ECD Corp.** capacitance meter.

Coating composition was evaluated using Fourier transform infrared spectroscopy with a Nicolet 7199 FTIR spectrometer in the reflection-absorption mode. A Harrick variable-angle, external reflection attachment was used at a 70° incident angle with a gold mirror for the background standard. Spectra were obtained at 4 cm^{-1} resolution; 256 interferograms were co-added before transforming with Happ-Genzel apodization. Representative samples were also evaluated using polarized light at different angles of incidence in order to deconvolute two overlapping bands representing aluminum oxide and an organic component.

Samples with visibly defective coatings were examined at 40x magnification using an optical microscope. The surface morphology of representative coatings which displayed good dielectric integrity was evaluated with a Hitachi S500 Scanning Electron Microscope (SEM). The cross-sections and thicknesses of these superior coatings were observed by first evaporating a thick ($\geq$ 1 μm) gold film over some of the anodic coatings to enhance the contrast, then mounting pieces sheared from the substrate edge-on in plugs of epoxy, and polishing these plugs. A thin layer of carbon was evaporated over the surface of these samples to reduce space charge accumulation. Secondary electron images were made. Energy dispersive spectra were collected during the time the samples were being evaluated in the SEM to identify some of the elements present in selected areas of the images.

*This model automatically stores and displays the maximum voltage applied with a response time of approximately 0.33 sec.

** ECD Corp., Cambridge, MA.

III. RESULTS

In general the performance of the ethanol mixtures which contained 20%, 60% and 90% water was substantially inferior to the performance of the 98% ethanol and 100% water mixtures. The 98% ethanol mixture performed acceptably over a broad range of processing parameters. The performance of the 100% water mixture was superior, provided certain considerations were observed at higher resistivity values which occur in conjunction with extended usage. Below, we describe in more detail the characteristics associated with each mixture.

A. Ethanol mixtures with 20%, 60% and 90% water.

In general, these mixtures displayed three failure modes:

1. Continual and dense scintillation* beginning at voltages on the order of 700-850 V that sometimes forced us to stop anodization before a cell voltage of 950 V had been reached.
2. Abnormally long processing times which approached eight hours.
3. Visibly flawed coatings.

These failure modes become more pronounced with increased electrolyte usage, or if the resistivity of the electrolyte is reduced to a value below 55 kΩ cm by adding more ammonium tartrate.

One clue that we generally observed which indicated anodic film growth was not proceeding well was a need for more coolant to maintain a certain temperature. Another clue was a strong ketone-like odor, which probably arose from the oxidation of the alcohol, that pervaded the laboratory.

The coatings that were produced by these electrolytes were, as a rule, visibly flawed, with many brown spots tracing out meandering breakdown tracks (Fig. 1).

---

*Scintillation can be described as faintly visible flashes of light over the surface of the coupon during anodization, usually in conjunction with bubbling, and whistling and hissing noises. It is initiated by localized flaws in the dielectric coating which lead to locally high electric fields, high current densities, and high temperatures, which, in turn, lead to the localized vaporization and ionization of the electrolyte, which can subsequently propagate larger flaws. This is not a desirable mode of operation.[6]

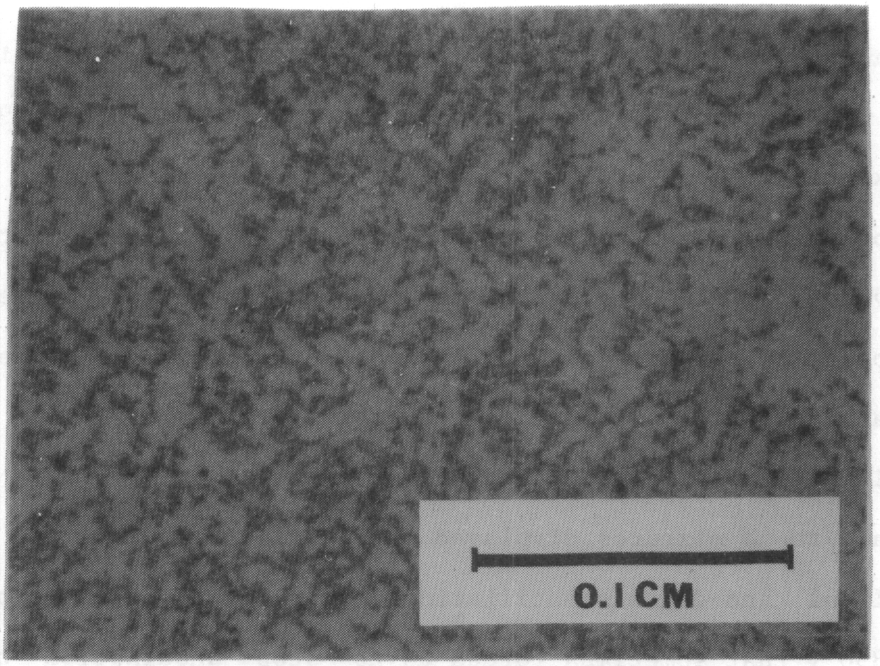


Fig. 1. Large flaws in a coating grown in an electrolyte mixture comprising 60% water, 40% ethanol. Continual and dense scintillations events were observed over the surface of this coupon during anodization.

The FTIR spectra (Fig. 2) of these coatings resemble the spectra displayed by the acceptable coatings which were produced by the 98% ethanol electrolyte, except for an assymmetry in a broad band at 680-750 cm^{-1} which is a superposition of a carboxylate bending vibration and an Aℓ-0 transverse optical lattice vibration; FTIR analysis with polarized light reveals that the assymmetry is probably due to a difference in the morphology of the $A\ell_2O_3$ in these samples.

The anions that are present in samples of the used 80%, 40% and 10% ethanol electrolytes, as determined by ion chromatography, are similar to the species found in samples of used 98% ethanol electrolyte: formate, tartrate, and acetate plus traces of oxalate.

It is interesting to note that the 90% water electrolyte performed as chaotically as the 20% and 60% water electrolyte until it had been used extensively. Then, one day, the ketone-like odor was gone, short processing times with little heating were achieved, and scintillation was not observed. Ion chromatography indicated that the low molecular weight formate and acetate species were missing

from this bath; FTIR indicated the amount of CO_2 entrained by these coatings was much lower than the amount of CO_2 incorporated in coatings produced earlier by this electrolyte. In summary, the performance of the 90% water electrolyte changed suddenly and resembled that of the 100% water electrolyte. It appeared as though the ethanol and its oxidative by-products had been fractionated or had been incorporated into earlier coatings.

B. 98% Ethanol and 100% Water Mixtures.

A cell voltage of 950 V and current decays to either 5% or 10% of the maximum current could be achieved reliably and reproducibly for each of these mixtures.

Ion chromatography indicated that the anion species present in samples of used electrolyte were significantly different for each mixture. Samples of both 98% ethanol electrolyte and 100% water electrolyte which had seen little use contained tartrate ions. The 98% ethanol mixture also contained substantial amounts of formate and acetate. The 100% water mixture contained oxalate. After extensive use, the water mixture contained little or no tartrate and small amounts of oxalate suggesting that oxalate and/or possibly formate are the species directly involved in anodic film formation.

Figs. 2b and c show FTIR spectra for the coatings produced by the 100% water and the 98% ethanol mixtures. The doublet at 1570 and 1470 cm^{-1} and part of the broad band at 680-750 cm^{-1} are due to entrained carboxylate groups. The 100% water coating spectra and the 98% ethanol coating spectra are very different with regard to the amount of CO_2 present (the 2343 cm^{-1} band). The water coatings contain approximately an order of magnitude less CO_2 than the 98% ethanol coatings.

Figure 3 presents SEM micrographs showing profiles of 98% ethanol and 100% water coatings which had been aged in to 0.1 mA/cm^2. Similar thicknesses ranging from 1.2-1.4 μm are produced by each electrolyte for all the electrolyte temperature schedules studied. The capacitance of all the 1 mm diameter dots

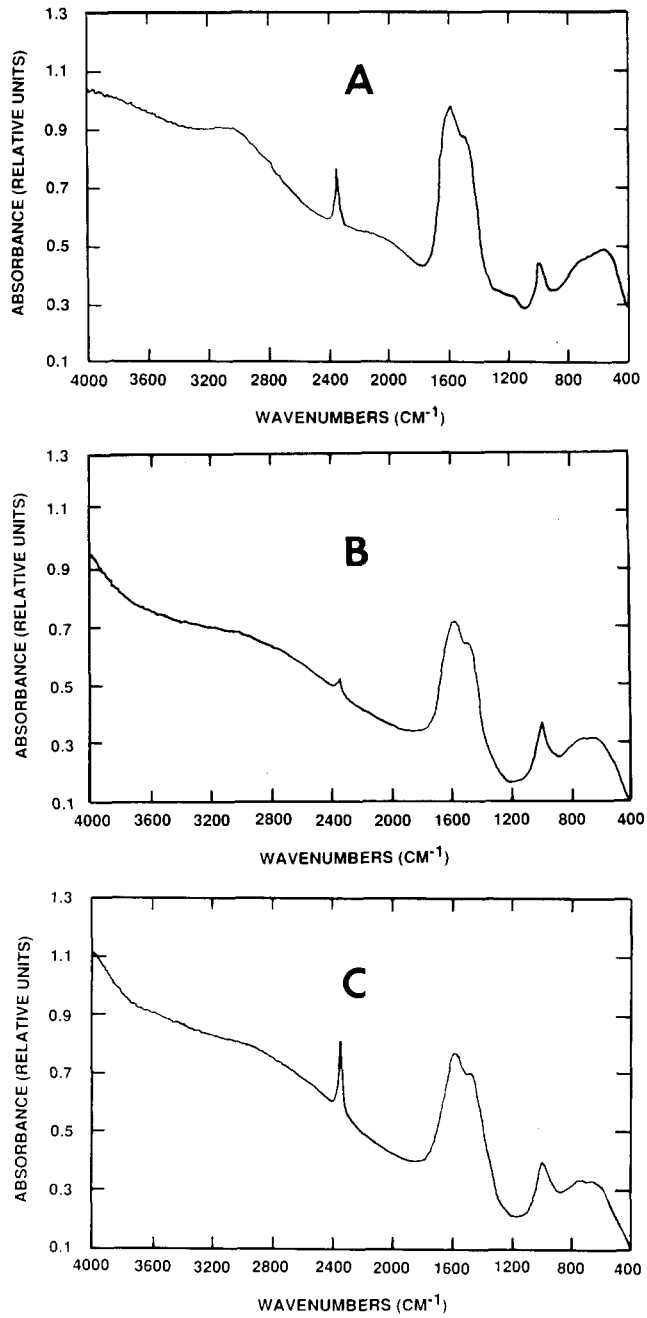


Fig. 2. FTIR spectra displayed by the anodic coatings. a. Coating formed in a 90% water 10% ethanol mixture. b. Coating formed in a 100% water mixture. c. Coating formed in a 98% ethanol mixture. Here the 2343 cm^{-1} band is assigned to physisorbed CO_2; the 1570 cm^{-1} and 1470 cm^{-1} doublet to a carboxylate group; the 950-980 cm^{-1} band to $A\ell_2O_3$; and the broad band at 680-750 cm^{-1} is assigned in part to a carboxylate bending vibration superimposed with a $A\ell$-O transverse optical lattice vibration.

tested falls within the range of 30.3-38.5 pF, with no discernable dependence on whether the coatings were formed in the 100% water or 98% ethanol electrolyte, or the temperature of the electrolyte. From the maximum and minimum values of coating thickness and capacitance, a dielectric constant that falls within the range of 6.3 ± 1.3 can be calculated for both the 98% ethanol and the 100% water coatings for all of the electrolyte temperature schedules studied.

Figure 4 shows the surface morphology of coatings grown in the 100% water electrolyte at 21-29°C (a, b, and c) and in the 98% ethanol electrolyte at 21-35°C (d).

Figure 4a shows a pit in the surface which is probably an artifact of an alloying component in the 6061-T6 aluminum alloy which was removed by the etchants used to prepare the substrates. The anodic coating tends to grow over the surface of the substrate and replicate these etch pits. Features similar to the one shown in 4a for a 100% water coating are also commonly observed for the 98% ethanol coatings. Figure 4b shows another type of surface feature that we observed for the 100% water coatings but not for the 98% ethanol coatings. It is a crystallite surrounded by amorphous material. The crystallite appears to have 6-fold rotational symmetry. Other researchers[7] have observed that amorphous aluminum oxide will crystallize locally when exposed to energetic events. Tetragonal (four-fold symmetric) γ-$A\ell_2O_3$ forms first at temperatures starting around 800°C. Hexagonal α-$A\ell_2O_3$ forms from γ-$A\ell_2O_3$ at an activation energy of 3.6 eV, or directly from the amorphous phase at temperatures above 1100°C. The presence of an electric field, as in anodization, would reduce the temperatures at which these crystalline phases would form. The electrochemical terminology for this effect is "field induced recrystallization."[6] The presence of these crystallites is generally believed to compromise the dielectric quality of a barrier anodic coating because the crystalline phases are more dense than the amorphous phase. The shrinkage which occurs when amorphous $A\ell_2O_3$ crystallizes leaves breakdown paths around the edges of the crystallites. The observation of the α-$A\ell_2O_3$-like

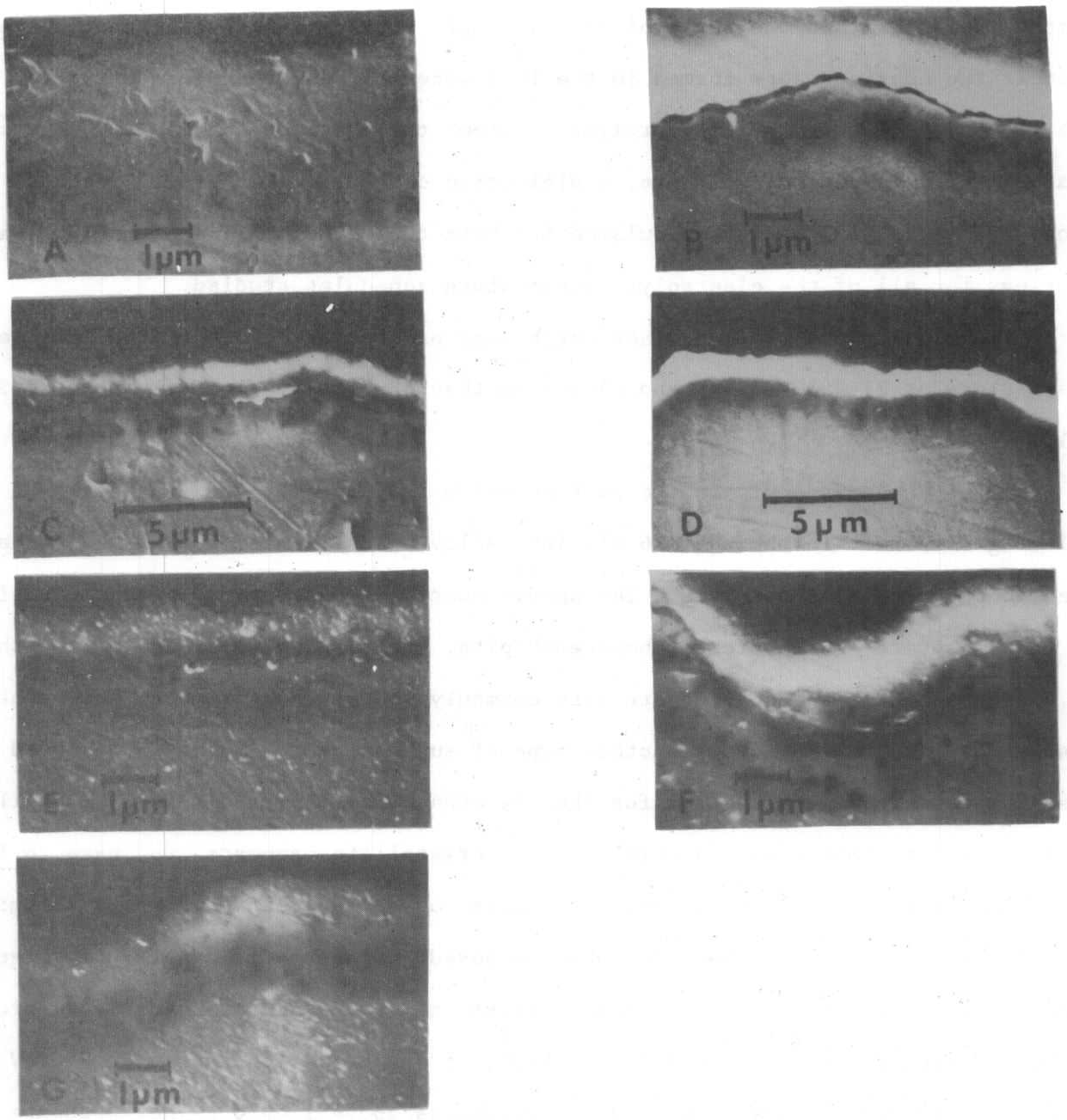


Fig. 3. SEM micrographs showing profiles which were used to determine the thicknesses of the coatings that were formed at 950 V and aged-in to 10% of the maximum current density. a. 98% ethanol at 18 ± 2°C - 1.2 μm. b. 98% ethanol at 21°C increasing to 35°C during the voltage rise, and 35°C decreasing to 21°C during the age-in-1.3 μm. c. 98% ethanol 21°C increasing to 35°C during the voltage rise and 35 ± 2°C during the age in-1.3 μm. d. 98% Ethanol 35 ± 2°C - 1.2 μm thick coatings. e. 100% water at 16 ± 2°C produces coatings that are 1.4 μm thick. f. 100% water at 25 ± 4°C - 1.4 μm thick coatings. 100% water at 33 ± 4°C - 1.2 μm thick coatings. The mottled, dark and light grey regions representing areas characterized by low electron emissivity is interpreted as being the barrier anodic layer. The brighter region of higher electron emissivity which appears to cover the anodic coatings in views a-e is aluminum rather than gold according to energy dispersive analysis. It may be an artifact of the sample preparation techniques that were used.

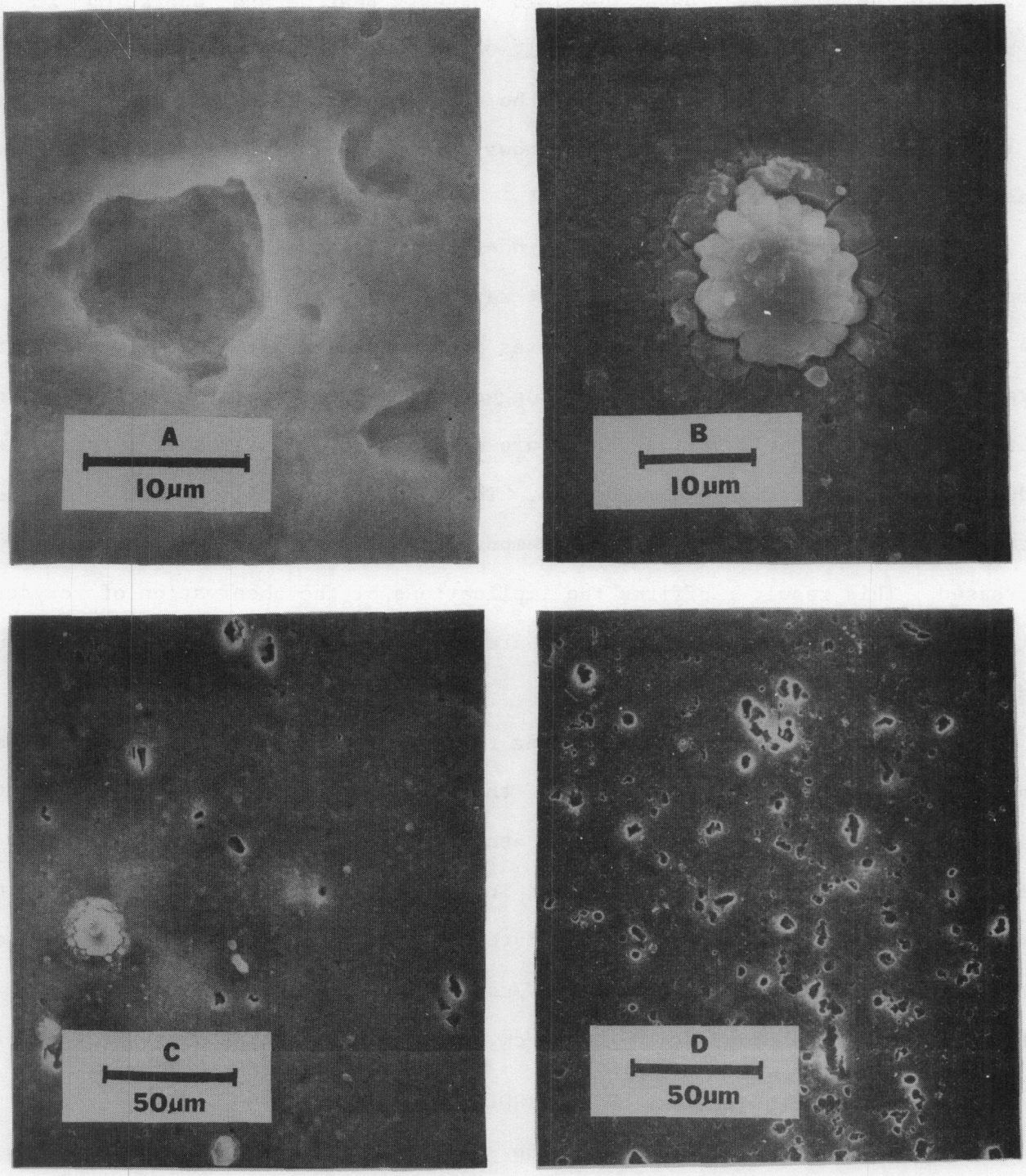


Figure 4. Surface morphologies of coatings imaged using transmission electron microscopy. a. Artifact of an alloying precipitate etch pit-100% water coating. b. Crystallite with 6-fold rotational symmetry-100% water coating. c. Micrograph taken at a lower magnification showing the relative abundance of these features for a 100% water coating. d. Similar magnification as shown in c, showing the relative abundance of etch pit artifacts and other flaws and the absence of crystallites for a 98% ethanol coating.

features in the 100% water based coatings suggests that we are operating at too high a temperature and/or too high a cell voltage for this electrolyte.[6]

Figures 4c shows the densities of the etch pit and crystallite features over a larger field of view. Figure 4d shows a comparable field of view for the 98% ethanol coatings.

Figure 5 shows histograms of processing time as a function of electrolyte temperature for the 98% ethanol and 100% water electrolytes.

The rate of anodic film growth increases as the 98% ethanol electrolyte temperature is increased; these observations suggest that we are operating this process at temperatures and cell voltages that are safely below the thresholds where field induced recrystallization causes damage. The rate of anodic film formation does not increase significantly as the temperature of the 100% water electrolyte is increased. This result reaffirms the implications of the observation of crystallites in these coatings: that we are operating beyond the ideal temperature and/or cell voltage for this process.

Even though we are not operating the 100% water electrolyte under optimal conditions, the dielectric properties of these coatings are substantially better than the coatings produced by the 98% ethanol electrolyte (Fig. 6). This may be due to the large amounts of CO_2 that are in the 98% ethanol electrolyte coatings compared to the 100% water electrolyte coatings. The dielectric breakdown strength of CO_2 is of the order of 10^5 V/cm; the dielectric breakdown strength of bulk $A\ell_2O_3$ is of the order of 10^6-10^7 V/cm. Entrained CO_2 appears to be more of a handicap than occasional α-$A\ell_2O_3$ formation is.

C. REPEATED USE OF THE 100% WATER ELECTROLYTE

Earlier studies[8] showed that the 98% ethanol electrolyte can be reused repeatedly in a production situation. This electrolyte operates over a broad range of resistivities and temperatures. In related studies, we reused this electrolyte extensively in the two 6ℓ parallel plate cathode anodic cells and in the 2 ℓ cylindrical cathode anodic cell successfully.

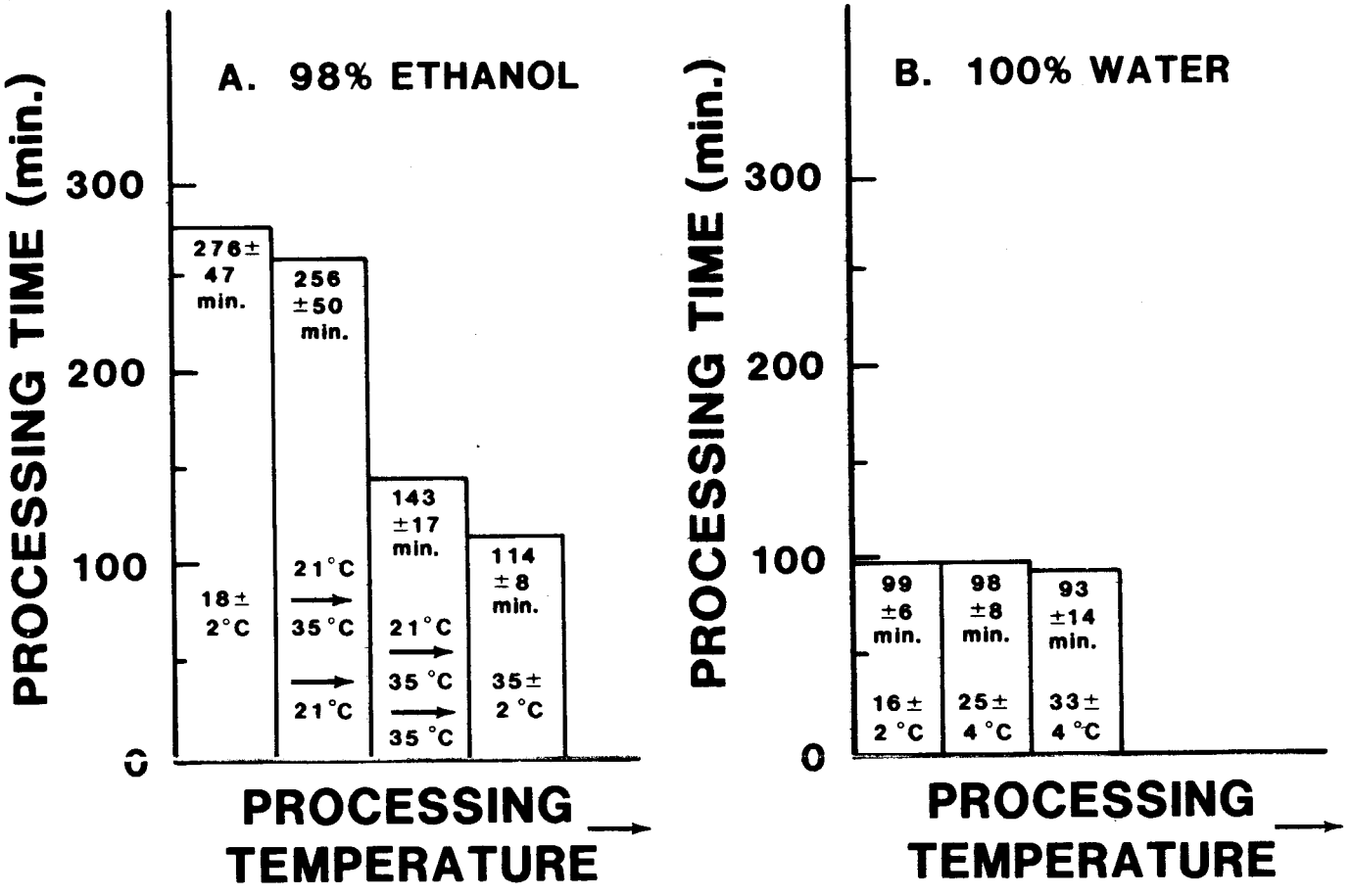


Fig. 5. Processing time for different electrolyte temperatures. a. 98% ethanol mixture. b. 100% water mixture.

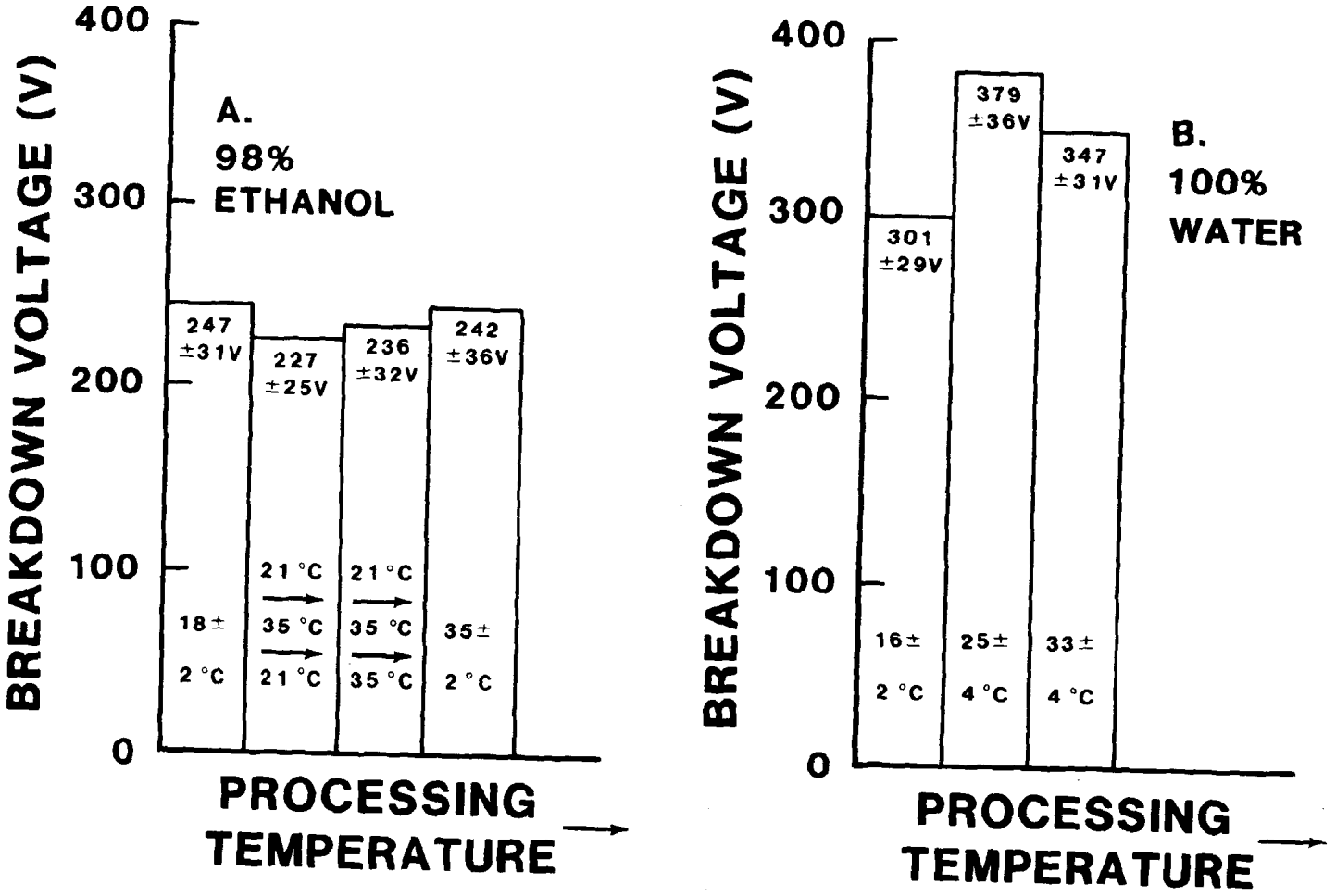


Fig. 6. Breakdown voltages exhibited by coatings formed at different temperatures. a. 98% ethanol coatings, b. 100% water coatings.

Preliminary studies indicate that the 100% water electrolyte can also be reused extensively when it is being used in the 6 ℓ cells with parallel plate electrodes (Figure 7).

However, problems soon occurred when we tried to reuse this electrolyte in the 2 ℓ cell with the cylindrical counterelectrode.

As this electrolyte is reused, the resistivity increases as anion species become incorporated into the anodic coating (Figure 7). Related earlier studies[8] indicate that these incorporated anion species improve the dielectric properties of the coatings; their presence tends to retard the crystallization of amorphous

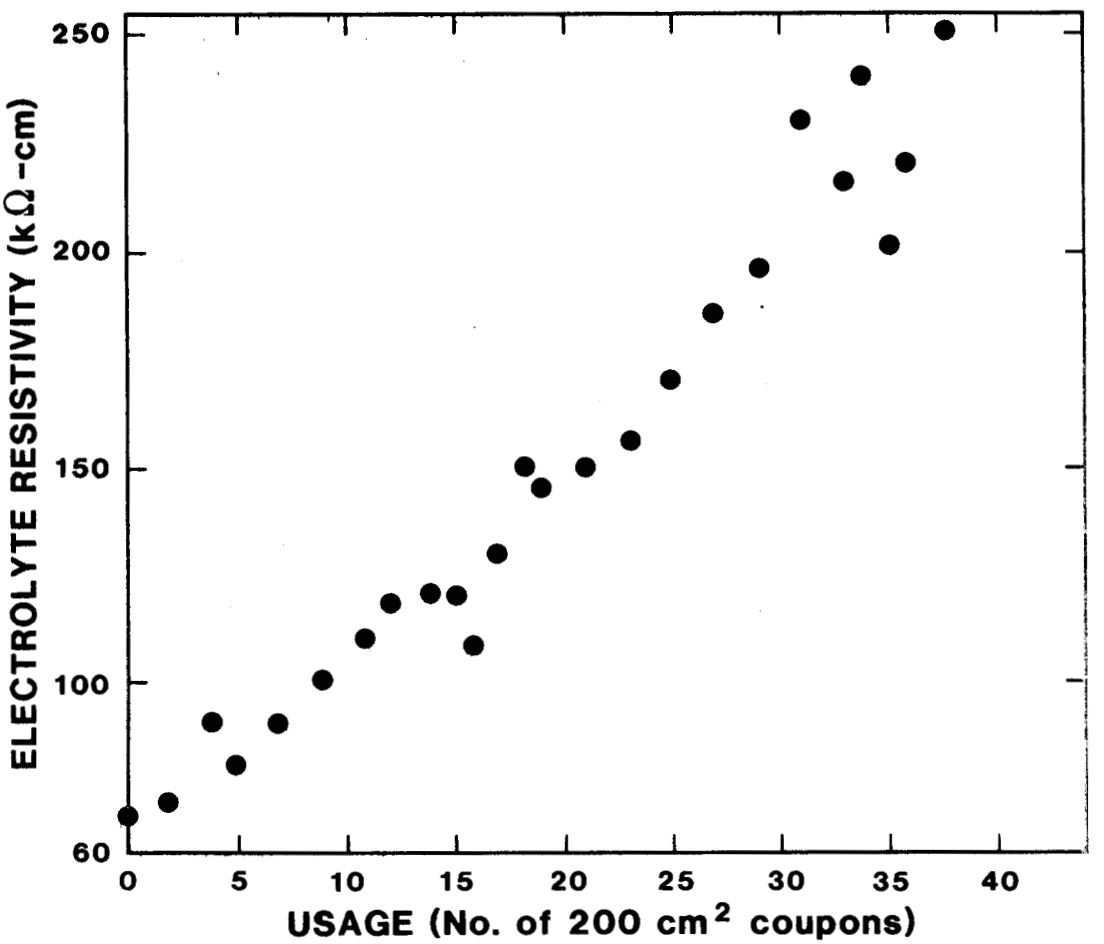


Fig. 7. Increase in the resistivity of the 100% water mixture as a function of repeated use. The coatings were grown on 10 x 10 cm^2 coupons at 950 V and aged-in to 0.05 mA/cm^2. Each coupon represents approximately 7.4 x 10^5 mA-sec passed through the 6 ℓ bath with parallel plate counterelectrodes.

Al_2O_3 under high electric field-high temperature conditions. We reused the 6ℓ parallel counterelectrode cell electrolyte extensively until the resistivity reached 250 kΩ-cm, and observed no significant variation in processing characteristics and coating quality if the temperature of the electrolyte was kept in the 21-27°C range. At resistivities above 150 kΩ-cm, however, problems occurred with the parallel counterelectrode geometry if the electrolyte temperature was allowed to exceed 30°C; extraordinarily long processing times, temporary increases in current density during age-in, abnormal electrolyte heating, and coatings with an undesirable brownish coloring resulted for these conditions. Similar problems occurred at lower resistivities (65 kΩ-cm) for the 100% water electrolyte in the 2 ℓ cylindrical counterelectrode cell. These problems could be minimized or avoided by adding more ammonium tartrate during processing. These processing problems which occur more readily for the 2 ℓ cylindrical geometry may be a manifestation of regionally high temperatures and/or regionally high electric fields which would occur at the edges of a coupon. Sharp edges are, in general, difficult to anodize because the coating at these sites is under more stress than it is at smoother areas of the substrate. In the parallel plate counterelectrode configuration, the electric fields at the edges of the coupons would be lower than the fields present at the coupon edges in the cylindrical counterelectrode geometry. The differences in the processing characteristics of the two types of geometries for the 100% water mixture compared to the 98% ethanol mixture suggest that it is more important to take care to shape the cathode to follow the geometry of the substrate for the 100% water electrolyte as compared to the 98% ethanol electrolyte if the operator wishes to work with high electrolyte resistivities (extensive reuse without "doctoring").

IV. DISCUSSION AND CONCLUSIONS

The characteristics of the five different electrolyte compositions can be summarized by three observations:

1. The superior performance of the 100% water electrolyte coatings despite the occurrence of field induced recrystallization and other behavior suggesting a vulnerability to locally high electric fields and/or temperatures.
2. The acceptable performance of the 98% ethanol electrolyte coatings with large amounts of entrained CO_2.
3. The inferior processing and coating properties associated with electrolytes that contain intermediate amounts of water and ethanol.

The above results suggest several conclusions with regards to the relative importance of various intrinsic properties of an electrolyte comprising ethanol, water, and ammonium tartrate.

The chemicals species that are chosen to prepare an electrolyte and their oxidative and dissociative by-products have a major effect on the properties of the anodic coatings which form. The CO_2 that is entrained in coatings formed from the electrolyte mixtures which contain ethanol is a major handicap.

Thermal conductivity and thermal capacity play a minor role. In principle, increasing the thermal conductivity and the thermal capacity of an electrolyte could be expected to help minimize the degradation that occurs in conjunction with scintillation and field induced recrystallization. In practice, thermal conductivity and thermal capacity increase as one goes from 98% to 80% to 40% to 10% ethanol, but processing becomes more difficult and the coatings produced are more flawed as one progresses from high to low ethanol concentrations.

This suggests that polarization plays an important role. Less polarization could be expected to occur in conjunction with the 98% ethanol mixture as compared to the 80%, 40%, and 10% mixtures. Less polarization in the vicinity of the double layer may tend to suppress scintillation and the degradative breakdown events which would otherwise occur at dielectric flaws caused by the entrained CO_2 that is generated by the ethanol. Less polarization in the double layer may result in the satisfactory performance of the 98% ethanol mixture.

The 100% water electrolyte currently appears to be the basis for a superior anodization process. The average processing time is approximately half the average processing time seen for the 98% ethanol electrolyte. The average breakdown voltage for the 100% water coatings is 50% higher than that observed for the 98% ethanol of coatings. Furthermore, the 100% water electrolyte does not contain expensive, controlled, or hazardous chemicals. It is reusuable, and it operates under moderate conditions without extensive or complicated auxilliary treatments. Additional work is necessary to identify the best cell voltages, resistivities, temperatures, and electrode geometry for operating this process.

REFERENCES

1. L. Young, Anodic Oxide Films, Academic Press, Ney York (1961).
2. John W. Diggle (ed.), Oxide and Oxide Films, 1 (1972), 2 (1973); John W. Diggle and Ashok K. Vijh (eds.), Oxide and Oxide Films, 3 (1976, 4 (1976); Ashok K. Vijh (ed.) Oxide and Oxide Films, 5 (1977), 6 (1981); Marcel Dekker Inc., New York, New York.
3. Janda K. G. Panitz and Donald J. Sharp, "Characterization of Procedure for Preparing 6061 Aluminum Alloy for Barrier Anodization," SAND82-1524, Sandia National Laboratories, Albuquerque, NM 87185 (1982).
4. D. J. Sharp and J. K. G. Panitz, J. Electrochem., Sec. 127 (1980) 1412.
5. R. M. Merrill, "Ion Chromatographic Procedures for the Analysis of Ethanol/Ammonium Tartrate Anodization Electrolyte," SAND82-1929, Sandia National Laboratories, Albuquerque, NM 87185 (1982).
6. W. D. Westwood, N. Waterhouse, and P. W. Wilcox, Tantalum Thin Films, Bell-Northern Research Ltd., Ottawa, Canada (1972). Ch. VI.
7. P. S. Sklad, "Proceedings of the 1986 Meeting of the Electron Microscopy Society of American," Albuquerque, NM.
8. J. K. G. Panitz, D. J. Sharp, R. M. Merrill, and D. M. Haaland, "Changes in a Barrier Anodization Process Observed in Conjunction with Electrolyte Usage," SAND82-2139, Sandia National Laboratories, Albuquerque, NM 87185 (1982).

DISTRIBUTION
Unlimited UC-25

1800	R. J. Eagan
1810	R. G. Kepler
1820	R. E. Whan
1821	S. H. Weissman
1821	R. M. Merrill (5)
1823	J. A. Borders
1823	K. J. Ward (6)
1830	M. J. Davis
1834	D. M. Mattox
1834	J. K. G. Panitz (5)
1840	R. E. Loehman, Actg.
1841	A. K. Hays
1841	D. J. Sharp (5)
3141	S. A. Landenberger (5)
3151	W. L. Garner (3)
3154-1	C. H. Dalin (8) for DOE/OSTI
5128	K. E. Mead
6221	L. C. Beavis
7473	T. P. Conlon
7473-3	F. E. Martinez (5)
7473-3	W. G. Yelton
8312	H. R. Johnson
8524	P. W. Dean